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# (54) Silicon based substrate with environmental/thermal barrier layer

(57) A barrier layer for a silicon containing substrate which inhibits the formation of gaseous species of silicon when exposed to a high temperature aqueous environment comprises a barium-strontium alumino silicate.

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[0013] Within the frame of the invention is the step of thermal spraying while holding the substrate at a temperature of between about 870°C to 1200°C. The coefficient of thermal expansion of the barrier layer is within ± 3.0 ppm/°C the coefficient of thermal expansion of the subtrate or ± 0.5 ppm/°C the coefficient of thermal expansion of the substrate.

[0014] Further advantages, characteristics and details of the invention are apparent from the following detailed description of preferred embodiments of the invention with reference to the attached drawing.

Figure 1 is a graph showing the stability of the barrier layer of the present invention with respect to recession and mass loss;
Figure 2 is a photomicrograph through a sample of the barrier layer of the present invention on a silicon carbide substrate;
Figure 3 is a photomicrograph of a sample of the barrier layer of the present invention applied to an intermediate layer on a silicon carbide substrate; and
Figure 4 demonstrates the effect of three specimens of the barrier layer of the present invention on weight loss in high temperature, aqueous environments.

[0015] The present invention relates to an article comprising a silicon containing substrate and a barrier layer, wherein the barrier layer inhibits the formation of gaseous species of silicon when the article is exposed to a high temperature, aqueous environment. The invention also relates to a method for producing the aforesaid article. In addition, it should be appreciated that while the barrier is particularly directed to an environmental barrier layer, the barrier layer also functions as a thermal barrier layer and thus the present invention broadly encompasses the use of environmental/ thermal barrier layers on silicon containing substrates and on substrates having comparable thermal expansion coefficients.

[0016] According to the present invention, the silicon containing substrate may be a silicon containing ceramic substrate or a silicon containing metal alloy. In a preferred embodiment, the silicon containing substrate is a silicon containing ceramic material as, for example, silicon carbide, silicon nitride, silicon carbon nitride, silicon oxynitride and silicon aluminum oxynitride. In accordance with a particular embodiment of the present invention, the silicon containing ceramic substrate comprises a silicon containing matrix with reinforcing such as fibers, particles, and the like and, more particularly, a silicon based matrix which is fiber-reinforced. Particularly suitable ceramic substrates are a silicon carbide coated silicon carbide fiber-reinforced silicon carbide particle and silicon matrix, a carbon fiber-reinforced silicon carbide matrix and a silicon carbide fiber-reinforced silicon nitride matrix. Particularly useful silicon-metal alloys for use as substrates for the article of the present invention include molybdenum-silicon alloys, niobium-silicon alloys, and other Si containing alloys having a coefficient of thermal expansion compatable with the barrier layer of the present invention.

[0017] Barrier layers particularly useful in the article of the present invention include alkaline earth metal aluminosilicates. In accordance with a preferred embodiment, barium aluminosilicates, barium-alkaline earth metal aluminosilicates and, particularly, barium-strontium aluminosilicates are preferred. In a particular embodiment, the barrier layer comprises from about 0.00 to 1.00 mole BaO, from about 0.00 to 1.00 mole of an oxide of a second alkaline earth metal, preferably SrO, about 1.00 mole $Al_2O_3$ and about 2.00 mole $SiO_2$. wherein the total of the BaO and the second alkaline earth metal or SrO is about 1.00 mole. The preferred barrier layer of the present invention comprises from about 0.10 mole to about 0.9 mole, preferably 0.25 to about 0.75 mole BaO, 0.1 mole to about 0.9 mole, preferably 0.25 to about 0.75 SrO, 1.00 mole $Al_2O_3$ and about 2.00 mole $SiO_2$ wherein the BaO and SrO total is about 1.00 mole. A particularly suitable barrier layer for use on silicon containing ceramic compositions in the article of the present invention comprises about 0.75 mole BaO, about 0.25 mole SrO, about 1.00 mole $Al_2O_3$, and about 2.00 mole $SiO_2$.

[0018] It is an important feature of the present invention to maintain compatibility between the coefficient of thermal expansion of the silicon containing substrate and the barrier layer. In accordance with the present invention it has been found that the coefficient of thermal expansion of the barrier layer should be within ± 3.0 ppm per degrees centigrade, preferably ± 0.5 ppm per degrees centigrade, of the coefficient of thermal expansion of the silicon containing substrate. When using a silicon containing ceramic substrate such as a silicon carbide or a silicon nitride matrix with or without reinforcing fibers as described above in combination with the preferred barium-strontium aluminosilicate barrier layer of the present invention, it is necessary to develop a stable crystallographic structure in the barrier layer of at least 50% by volume celsian in order to insure both structural integrity of the barrier layer and the desired thermal compatibility with respect to expansion coefficient between the silicon containing substrate and the barrier layer. The crystallographic structure of the barium-strontium aluminosilicate barrier layer is obtained as a result of preferred processing application and heat treating processing steps as will be described hereinbelow.

[0019] The barrier layer should be present in the article at a thickness of greater than or equal to about 0.5 mils (0.0005 inch), preferably between about 3 to about 30 mils and ideally between about 3 to about 5 mils. The barrier layer may be applied to the silicon based substrate by any suitable manner known in the art, however, it is preferable that the barrier layer be applied by thermal spraying as will be described hereinbelow.

[0020] In a further embodiment of the article of the present invention, an intermediate layer can be provided

silicon carbide is not stable to this environment and that the BSAS system is much more stable.

Example 2

[0029] Figure 2 is a cross section of a 4 mil thick BSAS of composition 0.75 BaO • 0.25 SrO • $Al_2O_3$ • 2 $SiO_2$ coating on SiC composite. The BSAS was thermal sprayed onto the silicon carbide composite using the following parameters:

| Parameter | Setting | |
|---|---|---|
| Plasma torch | Metco 3M | |
| Nozzle | GH | |
| Anode | std. | |
| Powder port | Metco #2 | |
| Primary gas | Ar@80 Metco gage | |
| Secondary gas | H2@8 Metco gage | |
| Substrate temp. | 850°C | |
| Carrier gas | Ar@37 Metco gage | |
| Powder feed | 15 to 25 gpm | |
| | Intermed. | Surface |
| Power | 30kw | 25kw |
| Stand-off | 2.5-3" | 5" |

[0030] Prior to coating the substrate was cleaned by grit blasting with 27 micron alumina particles at an impact velocity of 150 to 200 mps. As can be seen from Figure 2, the invention results in an excellent barrier layer structure.

Example 3

[0031] Figure 3 is a cross sectional view of a BSAS of composition 0.75 BaO • 0.25 SrO • $Al_2O_3$ • 2 $SiO_2$ barrier layer on a mullite/BSAS intermediate layer of 4±1 mils thickness on a silicon layer on silicon carbide composite. The coating was fabricated using the following parameters.

| | | | |
|---|---|---|---|
| Plasma torch | Metco 3M | | |
| Nozzle | GH | | |
| Anode | std. | | |
| Powder port | Metco #2 | | |
| Primary gas | Ar@80 Metco gage | | |
| Secondary gas | H2@8 Metco gage | | |
| Substrate temp. | 850°C | | |
| Carrier gas | Ar@37 Metco gage | | |
| Powder feed | 15 to 25 gpm | | |
| | Interface | Intermed. | Surface |
| Power | 25 kw | 30kw | 25kw |
| Stand-off | 4" | 2.5-3" | 5" |

or essential characteristics thereof. The present embodiment is therefore to be considered as in all respects illustrative and not restrictive, the scope of the invention being indicated by the appended claims, and all changes which come within the meaning and range of equivalency are intended to be embraced therein.

## Claims

1. An article comprising:

   a substrate comprising silicon; and
   a barrier layer, wherein the barrier layer inhibits the formation of gaseous species of Si when the article is exposed to a high temperature, aqueous environment.

2. An article according to claim 1 wherein the substrate is selected from the group consisting of silicon containing ceramic and metal alloys containing silicon.

3. An article according to claim 2 wherein the substrate is a silicon containing ceramic selected from the group consisting of silicon carbide, silicon nitride, and silicon aluminum oxynitride.

4. An article according to claim 2 wherein the substrate is a composite comprising a silicon based matrix and a reinforcing particle.

5. An article according to claim 4 wherein said substrate is selected from the group consisting of silicon carbide fiber-reinforced silicon carbide matrix, carbon fiber-reinforced silicon carbide matrix and silicon carbide fiber-reinforced silicon nitride.

6. An article according to claim 2 wherein said substrate is a silicon containing metal alloy selected from the group consisting of molybdenum-silicon alloys, niobium silicon alloys, iron-silicon alloys, and iron-nickel-silicon based alloys.

7. An article according to one of the claims 1 to 6 wherein the barrier layer comprises barium, especially barium oxide.

8. An article according to one of the claims 1 to 6 wherein the barrier layer comprises a barium aluminosilicate, especially a barium strontium aluminosilicate.

9. An article according to one of the claims 1 to 8 wherein the barrier layer comprises from about 0.00 to 1.00 moles BaO, from about 0.00 to 1.00 mole SrO, about 1.0 mole $Al_2O_3$ and about 2.00 mole $SiO_2$ wherein the total of BaO and SrO is about 1.00 mole.

10. An article according to one of the claims 1 to 8 wherein the barrier layer consists essentially of from about 0.00 to 1.00 mole BaO, from about 0.00 to 1.00 mole of an oxide of second alkaline earth metal about 1.00 mole $Al_2O_3$ and about 2.00 mole $SiO_2$ wherein BaO plus the other alkaline earth metal total 1 mole.

11. An article according to claim 9 wherein the barrier layer comprises from about 0.10 mole to about 0.90 mole BaO and from about 0.10 mole to about 0.90 mole SrO, preferably wherein the barrier layer comprises from about 0.25 mole to about 0.75 mole BaO and from about 0.25 mole to about 0.75 mole SrO.

12. An article according to claim 9 or 11 wherein the barrier layer comprises about 0.75 mole BaO and about 0.25 mole SrO.

13. An article according to claim 10 wherein the barrier layer comprises from about 0.10 mole to about 0.90 mole BaO and from about 0.10 mole to about 0.90 mole second alkaline earth oxide, preferably wherein the barrier layer comprises from about 0.25 mole to about 0.75 mole BaO and from about 0.25 mole to about 0.75 mole second alkaline earth oxide.

14. An article according to claim 10 or 13 wherein the barrier layer comprises about 0.75 mole BaO and about 0.25 mole second alkaline earth oxide.

15. An article according to one of the claims 8 to 14 wherein the crystallographic structure of the barrier layer is at least

34. A method according to one of the claims 29 to 33 including the step of preoxidizing the substrate to form a layer of $SiO_2$ prior to applying the barrier layer, wherein preferably the preoxidizing comprises heating the substrate at a temperature of between about 800°C to 1200°C for about 15 minutes to 100 hours.

35. A method according to one of the claims 24 to 34 including heat treating at a temperature of about 1250°c for about 24 hours, especially including the step of, after applying the barrier layer, heat treating the article at a temperature of about 1250°C for about 24 hours.

36. A method according to claim 33 including thermal spraying while holding the substrate at a temperature of between about 870°C to 1200°C.

37. A method according to claim 34 wherein the coefficient of thermal expansion of the barrier layer is within ± 3.0 ppm/°C the coefficient of thermal expansion of the substrate or wherein the coefficient of thermal expansion of the barrier layer is within ± 0.5 ppm/°C the coefficient of thermal expansion of the substrate.

38. A method according to one of the claims 29 to 37 wherein the barrier layer comprises from about 0.00 to 1.00 mole BaO, from about 0.00 to 1.00 mole SrO, about 1.00 mole $Al_2O_3$ and about 2.00 mole $SiO_2$ wherein the total of BaO and SrO is about 1.00 mole.

39. A method according to one of the claims 29 to 37 wherein the barrier layer consists essentially of from about 0.00 to 1.00 mole BaO, from about 0.00 to 1.00 mole of an oxide of second alkaline earth metal about 1.00 mole $Al_2O_3$ and about 2.00 mole $SiO_2$ wherein BaO plus the other alkaline earth metal total 1 mole.

40. A method according to one of the claims 29 to 38 wherein the barrier layer comprises from about 0.10 mole to about 0.90 mole BaO and from about 0.10 mole to about 0.90 mole SrO, especially wherein the barrier layer comprises from about 0.25 mole to about 0.75 mole BaO and from about 0.25 mole to about 0.75 mole SrO.

41. A method according to one of the claims 29 to 40 wherein the barrier layer comprises about 0.75 mole BaO and about 0.25 mole SrO.

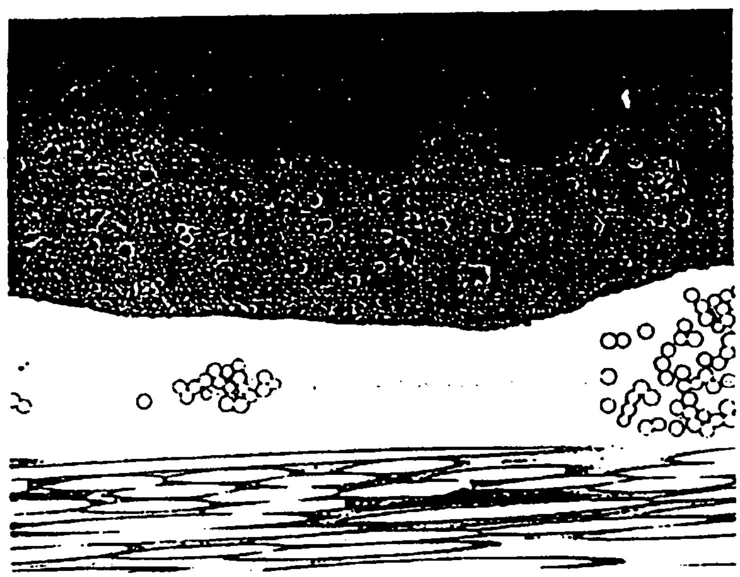

Fig. 2

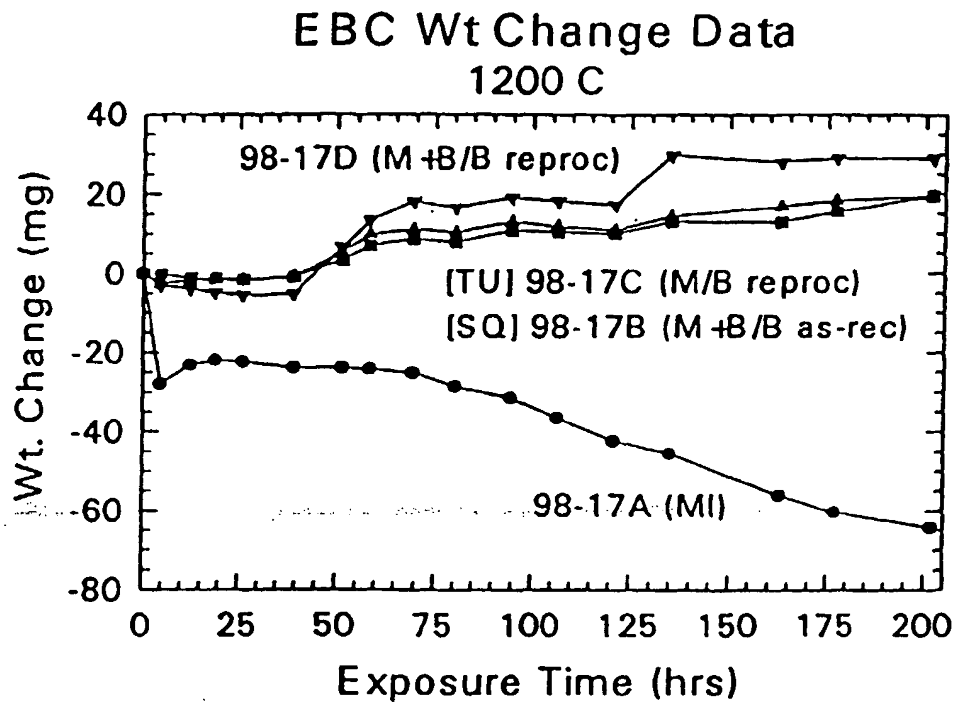
EBC Wt Change Data
1200 C
Wt. Change (mg)
40
20
0
-20
-40
-60
-80
0
25
50
75
100
125
150
175
200
Exposure Time (hrs)
98-17D (M+B/B reproc)
[TU] 98-17C (M/B reproc)
[SQ] 98-17B (M+B/B as-rec)
98-17A (M)

**Fig. 4**

## ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 00 10 8256

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22-08-2000

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